

What We Claim:

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Claims:

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- Sub A1
1. A hollow fiber porous membrane made of a perfluorinated thermoplastic polymer having an essentially skinless surface on at least one surface and an IPA flow time of less than about 3000 seconds.
  2. The membrane of Claim 1 wherein said membrane is asymmetric.
  3. The membrane of claim 1 or 2 wherein the IPA flow time is less than about 2000 seconds.
  4. The membrane of Claim 1 or 2 wherein the IPA flow time is less than about 1500 seconds
  5. The membrane of claim 1 or 2 wherein said perfluorinated thermoplastic polymer is poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) or poly(tetrafluoroethylene-co-hexafluoropropylene).
  6. The membrane of Claim 5, wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is propyl, methyl, or blends of methyl and propyl.
  7. A method of producing a hollow fiber porous membrane from a perfluorinated thermoplastic polymer having an essentially skinless surface on at least one surface comprising;
    - a) dissolving said perfluorinated thermoplastic polymer in a solvent that forms an upper critical solution temperature solution with said polymer,
    - b) extruding said solution through an annular die, a portion of said die being submerged in a cooling bath, and maintained at a temperature sufficiently high to prevent said solution from prematurely cooling,
    - c) ~~extruding~~ said solution into said cooling bath,

- 5 d) cooling said solution to below the upper critical solution temperature to cause separation into two phases by liquid-liquid phase separation, said phases being a polymer rich solid phase, and a solvent rich liquid phase, to form a gel fiber,
- 5 e) extracting said solvent from said gel fiber to form a porous hollow fiber membrane,
- f) drying said porous hollow fiber membrane under restraint.
- 10 8. The method of Claim 7 wherein said portion of said die being submerged is the die tip.
9. The method of Claim 7 wherein said perfluorinated thermoplastic polymer is dissolved in a concentration of from about 12% to about 35% by weight in a solvent that forms an upper critical solution temperature solution with said polymer.
- 15 10. The method of Claim 7 wherein step (b) comprises extruding said solution in an essentially horizontal attitude through an annular die, said die maintained at a temperature sufficiently high to prevent said solution from prematurely cooling, wherein the tip of said die penetrates through a wall separating said the body of said die from cooling bath, exposing the die exit to said cooling bath liquid.
- 20 11. The method of Claim 7 wherein the solvent has a boiling point lower than the temperature of the gel fiber at the die tip exit.
- 25 12. The method of Claim 7 wherein the solvent is a low molecular weight saturated chlorotrifluorohydrocarbon polymer.
- 30 13. The method of Claim 12 wherein the solvent is HaloVac® 80 or HaloVac® 56 or blends thereof.

14. The method of Claims 7, 8, 9, 10, 11, 12, or 13 wherein said perfluorinated thermoplastic polymer is poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) or poly(tetrafluoroethylene-co-hexafluoropropylene).
15. The method of Claim 14 wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is propyl, methyl, or of blends of methyl and propyl.
16. The method of Claims 7, 8, 9, 10, 11, 12, or 13 wherein said cooling bath liquid consists of a non-solvent for said perfluorinated thermoplastic polymer.
17. The method of Claim 14, wherein said cooling bath liquid consists of a non-solvent for said perfluorinated thermoplastic polymer.
18. The method of Claims 7, 8, 9, 10, 11, 12, or 13 wherein said cooling bath liquid consists of the group selected from silicone oil or dioctylphthalate.
19. The method of Claim 14, wherein said cooling bath liquid consists of the group selected from silicone oil or dioctylphthalate.
20. A hollow fiber porous membrane produced from a perfluorinated thermoplastic polymer having an essentially skinless surface on at least one surface, and a IPA flow time of less than about 3000 seconds produced by the method of Claims 7, 8, 9, 10, 11, 12, or 13.
21. The membrane of Claim 20 wherein said membrane is asymmetric.
22. The membrane of Claims 20 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) or poly(tetrafluoroethylene-co-hexafluoropropylene).

23. The membrane of Claim 22, wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of essentially all propyl, of essentially all methyl, or blends of methyl and propyl.
24. The membrane of Claim 21 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) or poly(tetrafluoroethylene-co-hexafluoropropylene).
25. The membrane of Claim 24, wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of essentially all propyl, of essentially all methyl, or blends of methyl and propyl.
26. A hollow fiber contactor membrane made of a perfluorinated thermoplastic comprising a porous surface on both diameters.
27. A hollow fiber contactor membrane made of perfluorinated thermoplastic comprising a unskinned surface both diameters capable of liquid-gas mass transfer with a Sherwood number equal to about 1.64 times the Graetz number to the 0.33 power in a range of Graetz numbers of from about 5 to about 1000.
28. The membrane of any one of Claims 26 and 27 wherein said perfluorinated thermoplastic polymer is selected from the group consisting of poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) and poly(tetrafluoroethylene-co-hexafluoropropylene).
29. The membrane of Claim 28 wherein the alkyl of said poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) is selected from the group consisting of propyl, methyl, and blends of methyl and propyl.